Photochemical Studies. XVIII.[1] Light-Induced Ring Expansion of Pyridine N-Oxides

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Irradiation of polyarylpyridine *N*-oxides results in ring expansion to 1,3-oxazepines in high yield and some deoxygenation to the parent amines. The 1,3-oxazepines were unambiguously identified by comparison with 2,4,5,7-tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine, the structure of which has been determined by X-ray crystallography. Irradiation of 2,3,5,6-tetraphenylpyridine *N*-oxide in benzene and ethanol at three different wavelengths is described.

The photochemistry of heteroaromatic amine *N*-oxides in general[3] and pyridine *N*-oxides in particular has been the subject of a number of recent studies.[3-8] However, both for the *N*-oxides in general and for the pyridine *N*-oxides a number of important questions have not yet been answered in a satisfactory way; *e.g.*, the exact nature of the excited states leading to photoproducts, substituent, solvent and wavelength effects on the product distribution, etc. We wish here to report and discuss the light-induced ring expansion of pyridine *N*-oxides, including some results obtained by varying the solvent and the wavelength.

Light-induced ring expansion of a variety of heteroaromatic *N*-oxides has been described and the structures of the ring-expanded products have been unambiguously determined by X-ray crystallography. Thus quinoline *N*-oxides give benz[*d*][1,3]oxazepines,[9,10] isoquinoline *N*-oxides give benz[*f*][1,3]oxazepines,[2] and quinoxaline *N*-oxides give benz[*d*][1,3,6]oxadiazepine,[11] etc.

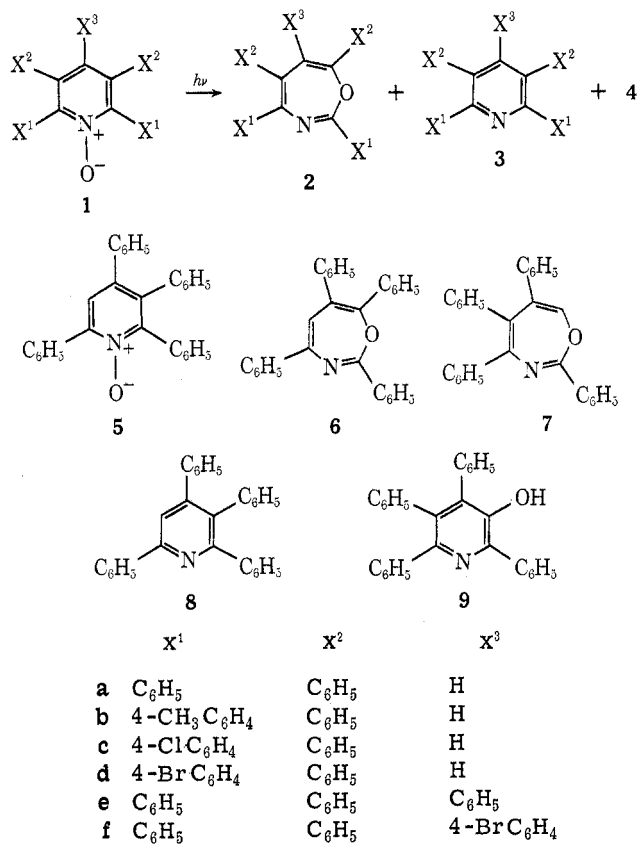
Aryl and cyano substituents on carbon atoms which become neighbors to the oxygen atom in the ring-expanded products have a strongly stabilizing effect on these.[3,9-11] Furthermore, when several routes of reaction are possible, the introduction of aryl groups tends to result in the predominance of one route. Consequently, we decided to examine aryl-substituted pyridine *N*-oxides.

Results

The classical method of obtaining pyridine *N*-oxides, *i.e.*, by oxidation of the parent amines with peroxy acids, turned out to be unpractical, and instead the substrates were prepared from the easily obtainable polyarylpyrylium salts and hydroxylamine.[12]

In a preliminary communication we reported that irradiation of 2,4,6-triphenylpyridine *N*-oxide gives a mixture of the parent amine, 2,4,6-triphenyl-3-hydroxypyridine, 2-benzoyl-3,5-diphenylpyrrole, and a substance which was tentatively believed to be 2,4,6-triphenyl-1,3-oxazepine.[13,14] At that time the assumed 2,4,6-triphenyl-1,3-oxazepine could not be obtained in the pure state, but more recently it was found that on preparative layer chromatography (plc) on silica gel impregnated with silver nitrate it could be purified. Due to lack of stability during the purification, the yield was very small, and therefore work with 2,4,6-triarylpyridine *N*-oxides was discontinued.

However, irradiation of the tetra- and pentaarylpyridine *N*-oxides (**1a-f**) led to the formation in high yields



	X¹	X²	X³
a	C_6H_5	C_6H_5	H
b	4-$CH_3C_6H_4$	C_6H_5	H
c	4-ClC_6H_4	C_6H_5	H
d	4-BrC_6H_4	C_6H_5	H
e	C_6H_5	C_6H_5	C_6H_5
f	C_6H_5	C_6H_5	4-BrC_6H_4

of the corresponding 1,3-oxazepines (**2a-f**) and minor amounts of the parent pyridines (**3a-f**). In the case of 2,3,5,6-tetraphenylpyridine *N*-oxide, minor amounts of

(1) For previous paper see ref 2.

(2) O. Simonsen, C. Lohse, and O. Buchardt, *Acta Chem. Scand.*, **24**, 268 (1970).

(3) For a recent review see G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

(4) J. Streith and C. Sigwalt, *Bull. Soc. Chim. Fr.*, 1157 (1970).

(5) M. Yamada and H. Arai, *Tetrahedron Lett.*, 2213, 2747 (1970).

(6) F. Bellamy, L. G. Ruiz Barragan, and J. Streith, *Chem. Commun.*, 456 (1971).

(7) C. Leibovici and J. Streith, *Tetrahedron Lett.*, 387 (1971).

(8) M. Ishikawa, C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron*, **25**, 295 (1969).

(9) O. Buchardt, B. Jensen, and I. Kjøller Larsen, *Acta Chem. Scand.*, **21**, 1841 (1967).

(10) B. Jensen, *Acta Crystallogr., Sect. B*, in press.

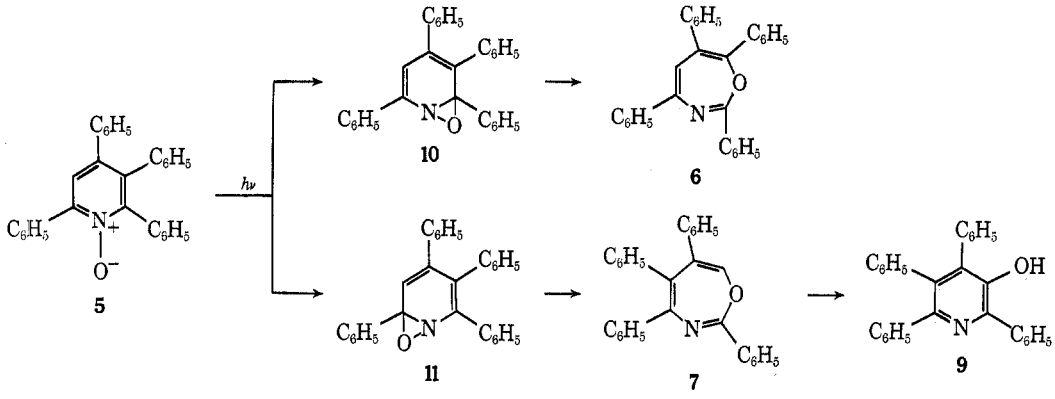
(11) O. Buchardt and B. Jensen, *Acta Chem. Scand.*, **22**, 877 (1968).

(12) C. L. Pedersen, N. Harrit, and O. Buchardt, *ibid.*, **24**, 3435 (1970).

(13) P. L. Kumler and O. Buchardt, *Chem. Commun.*, 1321 (1968).

(14) Independently it was found that irradiation of 2,6-dicyanopyridine *N*-oxide resulted in the formation of 2,6-dicyanopyridine, 5-cyano-2-pyrrolecarbonyl cyanide, and a compound believed to be 2,4-dicyano-1,3-oxazepine. Similar results were obtained for 2,6-dicyano-4-methylpyridine *N*-oxide.[8]

SCHEME I



an as yet unidentified compound **4** were also isolated (Table I). To obtain further information about the

TABLE I

IRRADIATION OF PYRIDINE N-OXIDES

Substrate	Wavelength, Å	Solvent	Product yields, % 2a	3a	4
	3500	Benzene	84–87	10–12	1–3
	3000	Benzene	78–83	14–15	2
	2537	Benzene	55–63	23–29	5–7
1a[a]	3500	Ethanol	75–76	13–19	3–4
	3000	Ethanol	77–83	13–14	4–5
	2537	Ethanol	71–75	17–20	4
	3500	Acetone	76–83	14–16	1–3
			2b	**3b**	
1b	3500	Benzene	78	19	
			2c	**3c**	
1c	3500	Benzene	87	9	
			2d	**3d**	
1d	3500	Benzene	83	17	
			2e	**3e**	
1e	3500	Benzene	80	17	
			2f	**3f**	
1f	3500	Benzene	76	20	

[a] These experiments have been repeated at least three times.

product distribution, 2,3,5,6-tetraphenylpyridine *N*-oxide (**1a**) was irradiated in various solvents with light of various wavelengths[15] (Table I).

Almost all the previously described experiments with pyridine *N*-oxides employed symmetrical substrates, whereby one complicating possibility of two pathways to products was eliminated. However, since the previous literature[4,16] indicates that one of the two possible pathways is favored (*vide supra*), it was deemed of interest to prepare and irradiate 2,3,4,6-tetraphenylpyridine *N*-oxide (**5**) (Scheme I). This resulted in the formation of a mixture of products which by plc was separated into a compound identified as 2,4,6,7-tetraphenyl-1,3-oxazepine (**6**), the parent amine (**8**), and a compound identified as 2,4,5,6-tetraphenyl-3-hydroxypyridine (**9**). When the crude reaction mixture was examined by nmr, no signals corresponding to compound **9** were observed. From the spectrum it was inferred that the mixture consisted of compound **8**, compound **6**, and 2,4,5,6-tetraphenyl-1,3-oxazepine (**7**), the two latter compounds being in the approximate ratio 2:3. We believe that

(15) Rayonet reactor, type RPR-208 with RUL 3500-, 3000-, or 2537-lamps.

(16) See ref 3, p 243.

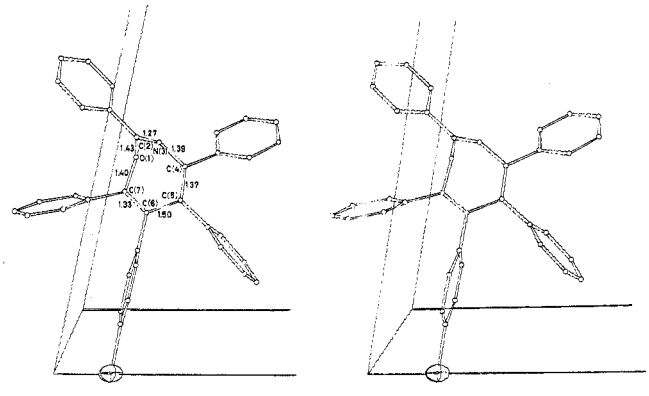


Figure 1.—A perspective view of 2,4,5,7-tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine (IIf). The atomic numbering and the bond lengths of the oxazepine ring are given. The bromine atom is represented by its thermal ellipsoid while the rest of the atoms are represented by spheres of an arbitrary size.

compound **7** rearranges to compound **9** during the purification procedure.[17]

Finally we wish to mention some preliminary results which indicate a pronounced heavy-atom effect. If 2,3,5,6-tetraphenylpyridine *N*-oxide (**1a**) is irradiated in tetrachloromethane, in ethylene bromide, and in methyl iodide with 3500-Å light the ratio of **2a** to **3a** decreases markedly in this order.

Structure Determination.—The 1,3-oxazepines were identified by comparison with 2,4,5,7-tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine (**2f**), which is the major photoproduct from 2,3,5,6-tetraphenyl-4-(4-bromophenyl)pyridine *N*-oxide (**1f**) (Table I). The structure of this oxazepine was unambiguously established by X-ray crystallography (Figure 1).[18] From Table II it will be seen that the ir spectra of the 1,3-oxazepines all show a characteristic absorption in the 1630-cm^{-1} region, while the uv spectra exhibit a characteristic absorption at *ca.* 380 nm, tailing into the visible region. Apparently the electron delocalization is of the same order of magnitude as that found in similar seven-membered ring compounds.[19]

2,4,6,7-Tetraphenyl-1,3-oxazepine (**6**) had the correct elemental analysis as well as the expected strong absorp-

(17) 2-Cyanobenz[*d*][1,3]oxazepines rearrange extremely easily to the corresponding 3-hydroxyquinoline; *cf.* ref 3, p 247, and C. Kaneko and S. Yamada, *Chem. Pharm. Bull.*, **15**, 663 (1967).

(18) The detailed X-ray structure determination will be published independently by B. Jensen, *Acta Crystallogr., Sect. B*, in press. We wish to acknowledge the excellent collaboration of Dr. Jensen.

(19) A. R. Katritzky, "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press, London, 1963, p 66.

TABLE II
CHARACTERISTIC SPECTROSCOPIC PROPERTIES OF 1,3-OXAZEPINES (2)[d]

Compd	Mp, °C	Ir,[a] cm^{-1}	Uv,[b] λ_{max}, nm (log ϵ)		Nmr,[c] τ	
					Aromatic	Vinylic
2a	195–196	1640	270 (4.54)	375 (3.97)	1.8–3.0	3.62
2b	211–212	1630	275 (4.57)	378 (4.03)	1.8–3.2	3.58
2c	194–196	1630	271 (4.61)	380 (4.05)	1.7–3.0	3.58
2d	213–215	1620	279 (4.60)	380 (4.00)	1.9–2.9	3.60
2e	245–246	1630	268 (4.42)	350 (3.85)	2.0–3.3	
2f	240–241	1630	270 (4.50)	350 (3.91)	2.0–3.5	

[a] In KBr discs. [b] In 96% EtOH. [c] In $CDCl_3$ with TMS as internal reference; methyl resonances in **2b** were 7.68 and 7.73. [d] Satisfactory analytical values (±0.3 for C, H, N) for all compounds were reported: Ed. Satisfactory analytical values for halogens for **2c**, **2d**, and **2f** were reported: Ed.

tion band in the ir (see Experimental Section). The nmr spectrum consisted of a multiplet at τ 1.87–3.14 and a singlet due to the single vinyl proton at τ 3.36, in the intensity ratio 20:1. However, the assumed 2,4,5,6-tetraphenyl-1,3-oxazepine (**7**) is less rigorously identified. The evidence for its presence is found in the nmr spectrum of the crude photolysis product from 2,3,4,6-tetraphenylpyridine *N*-oxide (**5**). This spectrum contained no signals from 2,4,5,6-tetraphenyl-3-hydroxypyridine (**9**), but consisted of a multiplet due to the aromatic protons, a singlet at τ 3.36 (from compound **6**), and a singlet at τ 3.68 (in the ratio 2:3); the latter singlet is assigned to the vinyl proton in compound **7**. Furthermore, the rearrangement of compound **7** to give compound **9** is also in agreement with the proposed structure (*vide infra*). 2,4,5,6-Tetraphenyl-3-hydroxypyridine was identified on the basis of elemental analysis and spectroscopy (see Experimental Section). The pyridines **3a–f** were identified by comparison with authentic samples (ir, melting point) prepared from pyrylium salts and aqueous ammonia.[20]

Discussion

The generation in high yields of stable 1,3-oxazepines requires a high degree of substitution with either aryl or cyano substituents, especially on carbons 2 and 7. Although this limits the types of 1,3-oxazepines which can be prepared by this method, it is nevertheless an excellent preparative method, leading to a hitherto unknown heterocyclic ring system. The X-ray data do not suggest any valence tautomerization to an oxaazanorcaradiene system.[18] An attempt to observe such a tautomerization by nmr spectroscopy at various temperatures was likewise unsuccessful.

Most evidence in the photochemistry of heteroaromatic amine *N*-oxides indicates that the deoxygenation mainly takes place from a triplet state, whereas the rearrangement mainly takes place from an excited singlet state.[4,6,21,22] Thus it has been found that triplet sensitization increases the extent of deoxygenation from 2-cyanopyridine *N*-oxide, whereas quenching with oxygen decreases the deoxygenation.[4,6]

When 2537-Å light is employed in benzene solution, energy transfer must take place *via* benzene. It is known that benzene can transfer singlet energy to olefins,[23] and we assume similar transfer to the *N*-oxide to occur, as well as triplet energy transfer. This phenomenon will be studied further. Our preliminary results with heavy atom solvents also indicate that the deoxygenation takes place from a triplet state and the rearrangements from an excited singlet state. However, the observed fact that decreasing the oxygen concentration present during irradiation of quinoline *N*-oxides[24–26] and 1,4-diphenylphthalazine *N*-oxide[27] decreases the photochemical deoxygenation seems to be in conflict with such a general mechanism.

We have previously proposed a mechanism for the formation of 1,3-oxazepines and 3-hydroxypyridines from pyridine *N*-oxides.[3] Only one bit of information in the literature indicates that the oxygen atom in an unsymmetrically substituted pyridine *N*-oxide can move in two directions upon irradiation, *i.e.*, the formation of both 2-methyl-3-hydroxypyridine and 6-methyl-3-hydroxypyridine in the photolysis of 2-methylpyridine *N*-oxide.[4,28] The presently described results with 2,3,4,6-tetraphenylpyridine *N*-oxide clearly demonstrate this duality in mechanism.

Since the 1,3-oxazepines can be obtained in very high yields, they are apparently quite photostable. Irradiation of the pure compounds substantiated this observation. With 3000- or 3500-Å light virtually no photoreactions took place. However at 2537 Å some photoreactivity was observed. No formation of the unidentified compound **4** was observed either in the photolysis or the thermolysis of 2,4,5,7-tetraphenyl-1,3-oxazepine.[29]

Experimental Section

Melting points (uncorrected) were determined on a Büchi melting point apparatus. Elemental analyses were carried out in the microanalysis laboratory of this university. Ir spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer, uv spectra on a Perkin-Elmer Model 137 uv spectrophotometer, and nmr spectra on a Varian A-60A spectrometer.

Chemicals.—All solvents were dried before use. All starting materials were reagent grade.

(20) R. Lombard and J.-P. Stephan, *Bull. Soc. Chim. Fr.*, 1458 (1958).
(21) C. Lohse, *J. Chem. Soc. B*, in press.
(22) We have previously suggested that the increased deoxygenation of 2,4,6-triphenylpyridine *N*-oxide in the presence of benzophenone was due to triplet sensitization.[18] However, this is probably rather due to a light-induced chemical action of benzophenone and ethanol; *cf.* J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 3995 (1970).
(23) (a) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 332 ff; (b) E. A. Andereesche, S. F. Kilin, I. Novotnyi, I. M. Rozinan, and F. Spurnyi, *Opt. Spectrosc.*, **24**, 117 (1965); (c) S. Sato, H. Kobayashi, and K. Fukano, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **72**, 209 (1969).
(24) M. Ishikawa, S. Yamada, H. Hotta, and C. Kaneko, *Chem. Pharm. Bull.*, **14**, 1102 (1966).
(25) O. Buchardt, C. Lohse, and P. L. Kumler, *Acta Chem. Scand.*, **23**, 159 (1969).
(26) C. Kaneko and S. Yamada, *Rep. Res. Inst. Dental Mater., Tokyo Medico-Dental Univ.*, **2**, 804 (1966).
(27) O. Buchardt, *Tetrahedron Lett.*, 1911 (1968).
(28) J. Streith, B. Danner, and C. Sigwalt, *Chem. Commun.*, 979 (1967).
(29) C. L. Pedersen and O. Buchardt, unpublished results.

Irradiations with an external light source were performed with a Rayonet reactor, type RPR-208, with RUL 3500-, 3000-, or 2537-Å lamps. The sample to be irradiated was stirred magnetically in a Pyrex flask (a quartz flask was used at 2537 Å). Irradiations with an internal light source were performed with a medium-pressure mercury arc, type Hanovia Q-700. The sample to be irradiated was placed in a water-cooled Pyrex container. All irradiations were performed at 25–35°.

Preparative layer chromatography was performed on 20 × 100 cm plates with a 2.5 mm thick layer of silica gel (Merck, $PF_{254-366}$). The plates were developed two times with a mixture of benzene and petroleum ether (bp 30–60°) (1:1). The fractions were scraped off the plates and isolated by extraction with chloroform in a Soxhlet apparatus.

Pyridine N-oxides were prepared according to the previously described method from the corresponding pyrylium salts.[12] 2,6-Di(4-methylphenyl)-3,5-diphenylpyridine N-oxide (**1b**) was prepared from 2,6-di(4-methylphenyl)-3,5-diphenylpyrylium bromide in 74% yield, mp 255–257°. *Anal.* Calcd for $C_{31}H_{25}NO$: C, 87.09; H, 5.89; N, 3.28. Found: C, 87.10; H, 5.95; N, 3.21. 2,6-Di(4-chlorophenyl)-3,5-diphenylpyridine N-oxide was prepared from 2,6-di(4-chlorophenyl)-3,5-diphenylpyrylium bromide in 76% yield, mp 249–251°. *Anal.* Calcd for $C_{29}H_{19}Cl_2NO$: C, 74.36; H, 4.09; N, 2.99; Cl, 15.14. Found: C, 74.25; H, 4.25; N, 2.97; Cl, 15.43. 2,6-Di(4-bromophenyl)-3,5-diphenylpyridine N-oxide was prepared from 2,6-di(4-bromophenyl)-3,5-diphenylpyrylium bromide in 95% yield, mp 248–249°. *Anal.* Calcd for $C_{29}H_{19}Br_2NO$: C, 62.50; H, 3.44; N, 2.51; Br, 28.68. Found: C, 62.35; H, 3.67; N, 2.50; Br, 28.72. 2,3,5,6-Tetraphenyl-4-(4-bromophenyl)pyridine N-oxide was prepared from 2,3,5,6-tetraphenyl-4-(4-bromophenyl)pyrylium bromide in 90% yield, mp 248–250°. *Anal.* Calcd for $C_{35}H_{24}BrNO$: C, 75.81; H, 4.37; N, 2.53; Br, 14.41. Found: C, 75.80; H, 4.47; N, 2.40; Br, 14.42. The above pyrylium salts were prepared by the previously described method.[30]

Pyridines were prepared from the corresponding pyrylium salts as previously described.[20] 2,6-Di(4-methylphenyl)-3,5-diphenylpyridine had mp 233–234°. *Anal.* Calcd for $C_{31}H_{25}N$: C, 90.47; H, 6.12; N, 3.40. Found: C, 90.13; H, 6.22; N, 3.34. 2,6-Di(4-chlorophenyl)-3,5-diphenylpyridine had mp 220–221°. *Anal.* Calcd for $C_{29}H_{19}Cl_2N$: C, 77.00; H, 4.23; N, 3.10; Cl, 15.67. Found: C, 77.10; H, 4.37; N, 2.98; Cl, 15.49. 2,6-Di(4-bromophenyl)-3,5-diphenylpyridine had mp 234–235°. *Anal.* Calcd for $C_{29}H_{19}Br_2N$: C, 64.34; H, 3.54; N, 2.59; Br, 29.53. Found: C, 64.30; H, 3.66; N, 2.50; Br, 29.37. 2,3,5,6-Tetraphenyl-4-(4-bromophenyl)pyridine had mp 224–226°. *Anal.* Calcd for $C_{35}H_{24}BrN$: C, 78.06; H, 4.50; N, 2.60; Br, 14.84. Found: C, 78.00; H, 4.56; N, 2.49; Br, 14.67.

Irradiation of Pyridine N-Oxides (1a–f, 5).—All irradiations in benzene solution were performed analogously to the following procedure. 2,3,5,6-Tetraphenylpyridine N-oxide (1.000 g) was dissolved in 400 ml of dry benzene and irradiated with an external light source for *ca.* 7 hr, the solvent was removed *in vacuo*, and the reaction mixture was separated by plc into 2,4,5,7-tetraphenyl-1,3-oxazepine (607 mg), 2,3,5,6-tetraphenylpyridine (84 mg), starting material (281 mg), and the unknown compound **4** (9 mg). This compound was difficult to separate from the pyridine. Its R_f value (eluent benzene–petroleum ether, 1:1) was marginally larger than the R_f of the pyridine. Irradiations in dry ethanol lasted for *ca.* 15 hr. In acetone 1.000 g of substrate was dissolved in 600 ml of acetone and irradiated for 12 hr. See Tables I and II.

The reaction mixture from the irradiation of 2,3,4,6-tetraphenylpyridine N-oxide (**5**) could be separated into 37% of 2,4,5,6-tetraphenyl-3-hydroxypyridine (**9**), 30% of 2,3,4,6-tetraphenylpyridine (**8**), and 30% of 2,4,6,7-tetraphenyl-1,3-oxazepine (**6**). However, from the tlc and nmr of the crude reaction mixture it could be seen that no compound **9** was present, but that the mixture consisted of compound **8** (tlc), compound **6** (nmr), and a compound believed to be **7** (nmr). Upon plc compound **7** disappeared and the hydroxypyridine **9** was isolated. 2,4,5,6-Tetraphenyl-3-hydroxypyridine had mp 210–211°. *Anal.* Calcd for $C_{29}H_{21}NO$: C, 87.19; H, 5.30; N, 3.51. Found: C, 87.30; H, 5.45; N, 3.55. Its ir spectrum showed a strong band at 3525 cm^{-1} (OH); its nmr ($CDCl_3$) showed a multiplet at τ 1.84–3.33 and a singlet at τ 4.88 (OH). This signal disappeared upon shaking with D_2O. 2,4,6,7-Tetraphenyl-1,3-oxazepine had mp 136–139°. *Anal.* Calcd for $C_{29}H_{21}NO$: C, 87.19; H, 5.30; N, 3.51. Found: C, 86.77; H, 5.60; N, 3.43. Its ir spectrum showed a strong absorption at 1615 cm^{-1}; its nmr ($CDCl_3$) showed a multiplet at τ 1.87–3.14 and a singlet due to the vinyl proton at τ 3.36, in the ratio 20:1.

Preparative Scale Synthesis of 2,4,5,7-Tetrahenyl-1,3-oxazepine (2a).—2,3,5,6-Tetraphenylpyridine N-oxide (2.00 g) was dissolved in dry benzene (280 ml) and irradiated with an internal light source until no more starting material could be detected by tlc. The solvent was removed and the residue was recrystallized from hexane to give 2,4,5,7-tetraphenyl-1,3-oxazepine (1.57 g, 79%).

Irradiation of 2,4,6-Triphenylpyridine N-Oxide.—This was undertaken as previously described.[13] Only by tlc on a mixture of silica gel and silver nitrate (98:2) could we separate the 2,4,6-triphenylpyridine and the 2,4,6-triphenyl-1,3-oxazepine. The silver nitrate, however, caused partial decomposition of the latter (*ca.* 50% per elution), which no attempt was made to overcome. The two separated products exhibited the spectral patterns (ir and nmr) attributed to them in the mixture.[13]

Registry No.—**1b**, 35358-95-3; **1c**, 35358-96-4; **1d**, 35358-97-5; **1f**, 35358-98-6; **2a**, 35358-99-7; **2b**, 35359-00-3; **2c**, 35359-01-4; **2d**, 35359-02-5; **2e**, 35359-03-6; **2f**, 35359-04-7; **3b**, 35359-05-8; **3c**, 35359-06-9; **3d**, 35359-07-0; **3f**, 35427-22-6; **6**, 35359-08-1; **7**, 35359-09-2; **8**, 3558-63-2; **9**, 35359-10-5.

(30) M. Simalty and J. Caretto, *Bull. Soc. Chim. Fr.*, 2959 (1966).